REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
09-09-2013	Book Chapter	

4. TITLE AND SUBTITLE
Mechanophores for Self-Healing Applications

5a. CONTRACT NUMBER
W911NF-07-1-0409

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611103

6. AUTHOR(S)
Charles E. Diesendruck, Jeffrey S. Moore

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Illinois - Urbana
Board of Trustees of the University of Illinois
1901 S First Street
Champaign, IL 61820 -7473

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
52530-CH-MUR.59

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

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15. SUBJECT TERMS
sustainable materials, self-healing, mechanochemistry, stress-responsive

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Jeffrey Moore
UU	UU	UU	UU		19b. TELEPHONE NUMBER *(include area code)* 217-244-5289

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

Report Title

10.1002/9783527670185.ch8

ABSTRACT

The transformation of chemical energy into mechanical energy is elementary in our lives, not only moving cars and airplanes, but pumping blood in our bodies and moving our eyeballs as we read these lines. The reverse action, defined as mechanochemistry [1–3], is to make chemical transformations using mechanical force, and finding simple examples may be challenging for people unfamiliar with the subject.

Certainly one can think of petroleum or diamonds as examples. Millions of years of small chemical changes under high pressure produced these valuable materials, but more elementary examples are necessary in order to study these transformations. Indeed, the first reported example of mechanochemistry was demonstrated by Staudinger in the 1930s, where he demonstrated that masticating a polymeric material caused not only the expected conformational and positional changes in the polymer chains, but it also cleaved covalent chemical bonds, causing a decrease in the molecular weight of the polymer [4–6]. Indeed, this phenomenon was studied in the rubber industry, revealing that when rubber was masticated in the presence of oxygen (from air), the rubber would “soften”, while in the absence of oxygen the rubber properties would not change [7]. The explanation suggested then was based on the homolytic cleavage of cross-linking bonds to produce two radicals. In the absence of oxygen these radicals recombine and reform cross-linking bonds, restoring the properties of the material; on the other hand, if oxygen is present the radicals are quenched as peroxyl radicals and the cross-linking bonds are lost, causing the material to soften [8]. Remarkably, one of the first studies in mechanochemistry provided a synthetic self-healing material, demonstrating the broad potential technologies that could evolve from this science. In order to understand the effect of mechanical stress in materials, it was necessary to study the changes at the molecular level, in addition to examining macroscopic properties. The analytical challenge of looking at few chemical changes in macromolecules was unrealistic at the time, and was achieved only several years later. For example, the hypothesis that the chemical bonds broke homolytically was directly demonstrated only in the 1960s, using electron spin resonance (ESR) to study mechanically damaged materials [9]. An important step to ease the study of mechanochemistry of polymers was the development of mechanical stressing in solution, where chemical changes are distributed homogeneously through the chains. Moreover, classical analytical
chemistry methods to analyze the chemical changes, such as spectrometers, laser light scattering and others could be used, giving the possibility to study molecular weight change and kinetics of the mechanochemical reactions. This important breakthrough came early and was achieved through the use of flow fields [10] and ultra-sound cavitation that caused high shear stress on the chains through flow
induced elongation [11]. A key discovery that came from the study in solution was the observation that certain bonds cleave more easily than others [12]. If one of these bonds is present in the main chain, close to its center (Figure 8.1), it can be selectively cleaved. This originated the concept of mechanophores bonds or chemical functionalities that are especially susceptible to undergoing a chemical change caused by mechanical stress. Mechanophores, when placed into a polymeric molecule where the mechanical force is highest, selectively undergo a chemical reaction [13]. In this chapter we will describe how polymeric materials deal with mechanical stress, methods to mechanically stress materials in a controlled manner to study the chemical changes, and the development of mechanophores that direct mechanical energy to molecular constituents to produce positive effects on the material, such as self-healing.

8
Mechanophores for Self-Healing Applications

Charles E. Diesendruck and Jeffrey S. Moore

8.1
Introduction

The transformation of chemical energy into mechanical energy is elementary in our lives, not only moving cars and airplanes, but pumping blood in our bodies and moving our eyeballs as we read these lines. The reverse action, defined as mechanochemistry [1–3], is to make chemical transformations using mechanical force, and finding simple examples may be challenging for people unfamiliar with the subject.

Certainly one can think of petroleum or diamonds as examples. Millions of years of small chemical changes under high pressure produced these valuable materials, but more elementary examples are necessary in order to study these transformations. Indeed, the first reported example of mechanochemistry was demonstrated by Staudinger in the 1930s, where he demonstrated that masticating a polymeric material caused not only the expected conformational and positional changes in the polymer chains, but it also cleaved covalent chemical bonds, causing a decrease in the molecular weight of the polymer [4–6]. Indeed, this phenomenon was studied in the rubber industry, revealing that when rubber was masticated in the presence of oxygen (from air), the rubber would "soften", while in the absence of oxygen the rubber properties would not change [7]. The explanation suggested then was based on the homolytic cleavage of cross-linking bonds to produce two radicals. In the absence of oxygen these radicals recombine and reform cross-linking bonds, restoring the properties of the material; on the other hand, if oxygen is present the radicals are quenched as peroxyl radicals and the cross-linking bonds are lost, causing the material to soften [8]. Remarkably, one of the first studies in mechanochemistry provided a synthetic self-healing material, demonstrating the broad potential technologies that could evolve from this science.

In order to understand the effect of mechanical stress in materials, it was necessary to study the changes at the molecular level, in addition to examining macroscopic properties. The analytical challenge of looking at few chemical changes in macromolecules was unrealistic at the time, and was achieved only several years later. For example, the hypothesis that the chemical bonds broke homolytically

Self-Healing Polymers: From Principles to Applications, First Edition. Edited by Wolfgang H. Binder.

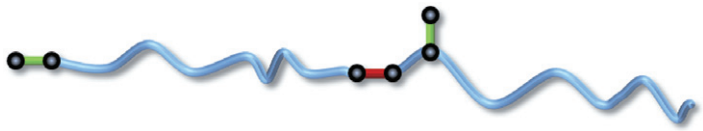


Figure 8.1 Possible positioning of mechanophores: chain end, side chain, and chain center. Activation is highest when the mechanophore is at the chain center and the polymer chain passes through both ends of the activated bond.

was directly demonstrated only in the 1960s, using electron spin resonance (ESR) to study mechanically damaged materials [9].

An important step to ease the study of mechanochemistry of polymers was the development of mechanical stressing in solution, where chemical changes are distributed homogeneously through the chains. Moreover, classical analytical chemistry methods to analyze the chemical changes, such as spectrometers, laser light scattering and others could be used, giving the possibility to study molecular weight change and kinetics of the mechanochemical reactions. This important breakthrough came early and was achieved through the use of flow fields [10] and ultra-sound cavitation that caused high shear stress on the chains through flow induced elongation [11].

A key discovery that came from the study in solution was the observation that certain bonds cleave more easily than others [12]. If one of these bonds is present in the main chain, close to its center (Figure 8.1), it can be selectively cleaved. This originated the concept of mechanophores – bonds or chemical functionalities that are especially susceptible to undergoing a chemical change caused by mechanical stress. Mechanophores, when placed into a polymeric molecule where the mechanical force is highest, selectively undergo a chemical reaction [13].

In this chapter we will describe how polymeric materials deal with mechanical stress, methods to mechanically stress materials in a controlled manner to study the chemical changes, and the development of mechanophores that direct mechanical energy to molecular constituents to produce positive effects on the material, such as self-healing.

8.2 Mechanochemical Damage

8.2.1 Deformation

The response of a polymeric material to mechanical stress depends on its chemical composition as well as the chain architecture [14]. The primary mechanism used by a material to dissipate mechanical energy is through deformation, including displacement of chains as a group or in relation to each other, as well as conformational changes. Thermoplastic polymers (linear or branched chains which are

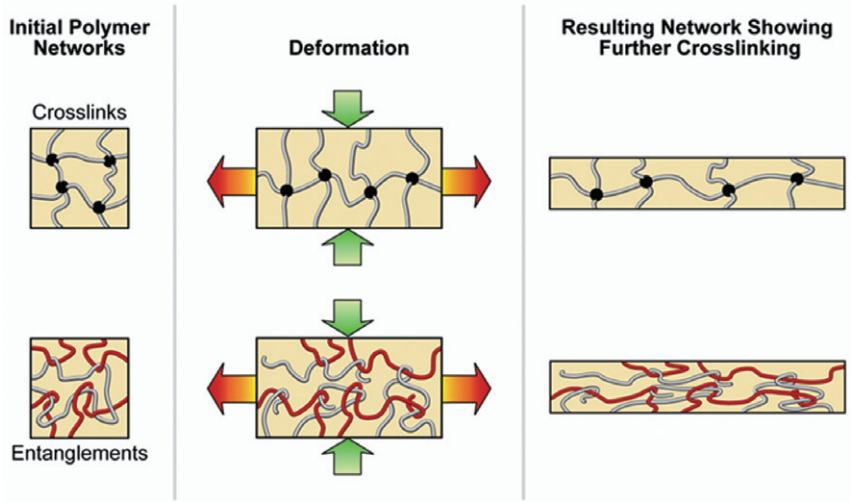


Figure 8.2 Deformation of polymers in the solid state (above T_g) [1]. Reprinted with permission from reference [1]. Copyright 2009 American Chemical Society.

entangled in the solid state) may undergo permanent displacement of chains, while in thermosets (cross-linked polymers) this displacement may be limited due to covalent constraints (Figure 8.2). The chemical composition defines the non-covalent interactions between chains and the feasibility of energy dissipation through conformational changes, but other factors are also very influential: molecular mass, density of chain entanglements/cross-linkages, chain alignment, and degree of crystallinity.

Non-covalent forces between chains, such as van der Waals forces, hydrogen bonds and electrostatic interactions determine the ease by which the chains move independently. Calculating the energy of these interactions for a specific chain or chain segment is very complicated, and mostly unnecessary. The macroscopic effect of these interactions is clearly observed by studying the glass transition temperature (T_g) and melting point of the polymeric material, both of which can be used as a method to compare between materials and their ability to dissipate mechanical energy through displacement of chain segments.

Above the T_g the polymer chains present more mobility, facilitating their displacement and increasing their ability to dissipate mechanical force. On the other hand, below the T_g the mobility is restricted and the polymer behaves like an elastic solid, that is, strain energy is reversibly stored in the polymer until the chains finally deform irreversibly, as in viscous flow [15]. In the solid state, stress on particular polymer chains is mainly localized in the entanglements or cross-links in the material [16] and, above a certain stress, more energetic movements become significant in the dissipation of the concentrated stress.

The second, more energetic way polymer chains dissipate energy is by intramolecular geometry changes. There are three internal motions by which molecules

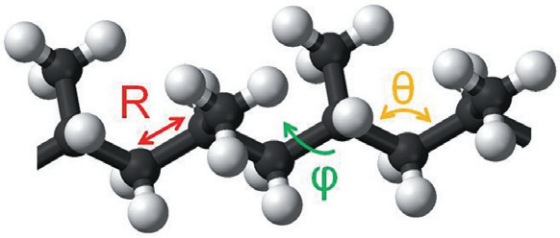


Figure 8.3 Different directions for force dissipation at the molecular level: rotation of dihedral angles φ, bending of bond angles θ, and stretching of bond length R.

deform when acted upon by mechanical force: rotation of dihedral angles, bending of bonds, and stretching of bonds (Figure 8.3).

The effect of mechanical force on the molecular geometry was studied by infrared (IR) spectrometry of polypropylene [17]. Using a polarizer to examine parallel and perpendicular dichroic bands, and analyzing first-order peak shift and difference spectra, this seminal work was able to simultaneously verify the changes in these three parameters and quantitatively compare them. As expected, the change in dihedral angle ($\Delta\varphi$), being the easiest deformation, underwent the steepest change, up to 9 times more than the changes observed in bond length (ΔR), while valence angle bending ($\Delta\theta$) was around 2.4 times the change in bond length. The authors were also able to show that these changes could be significantly different for different C–C bond types. For example, axial bonds were more easily stretched than equatorial bonds. This indicates that the conformation, which changes under mechanical force, is an important factor in this method of energy dissipation.

8.2.2 Homolytic Bond Cleavage

When high stress is applied to a material, chemical bond stretching becomes a significant method for dissipating this energy. The potential caused by mechanical stretching, when added to the original Morse potential, changes the energy versus distance relationship (Figure 8.4). Above a certain stress level, bonds may stretch to a distance where the interaction between the electronic orbitals of the two atoms becomes negligible, leading to the cleavage of the bond.

Most bond cleavages caused by stretching are homolytical in nature, as demonstrated by the presence of radicals [9]. Radicals have high chemical potential and are unstable. They dissipate their potential through several pathways, such as recombination, disproportionation, reaction with atmospheric oxygen, or reacting with another chemical bond. Sonication experiments of polymers in the presence of spin traps demonstrated the creation of radicals in solution using UV–Vis spectroscopy [18, 19]. This indirect method to observe bond cleavage turned out to be very useful, and was one of the first means to study mechanochemical kinetics.

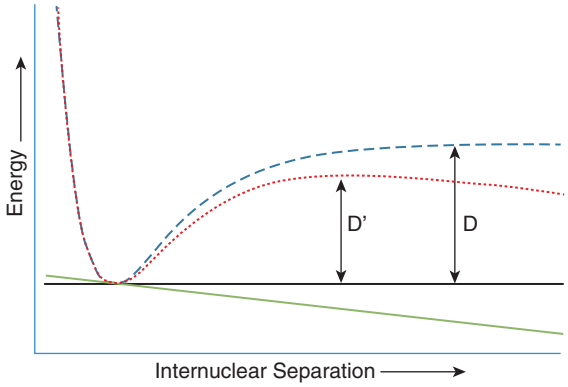


Figure 8.4 Energy as a function of intermolecular distance. Normal Morse potential (blue), potential owing to mechanical force (green) and sum of the potentials (red). The dissociation energy *D* is changed by the mechanical force to *D*' [8].

The high reactivity of the radicals produced under mechanical force can be used for productive chemistry. For example, they were used as radical initiators for polymerization, creating co-polymers [20], or used as an effective method to produce H_2O_2 [21]. In special cases, they can even recombine, healing the broken bond (with heat being released).

8.2.3
Heterolytic Bond Cleavage

Homolytic bond cleavage is the generally accepted mechanism when high stress is applied to polymers, and it was demonstrated by direct and indirect detection methods. Heterolytic bond cleavage, while not demonstrated directly, appears occasionally as a proposed mechanism, especially for the cleavage of supramolecular bonds, and when bonds are cleaved in a rearrangement reaction. For example, in the widely studied spiropyran–merocyanine rearrangement by mechanical force [22, 23], the carbon–oxygen bond is cleaved into a phenolate, that is, the oxygen takes both the electrons. In polymers containing coordinating organometallic systems (described below), the ligand is cleaved supposedly taking both the electrons. A molecular dynamics study also proposed that heterolytic bond cleavage may become a major factor when functional groups stabilizing the produced ions are interacting with one of the atoms in the stretched bond [24]. In this study, water molecules interacted through hydrogen bonds with the non-bonding electrons of the oxygen in PEG chains, and the calculations indicated a preference towards heterolytical bond cleavage. One can imagine that other functional groups in polymer side-chains may cause similar effects, but a direct experimental demonstration of this effect has not been reported.

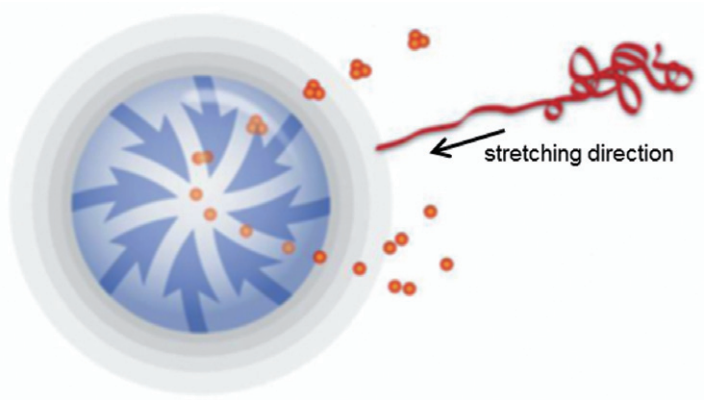


Figure 8.5 Implosion of cavitation bubble pulling the solvent and polymer towards it. Reprinted with permission from reference [1]. Copyright 2009 American Chemical Society.

8.3 Activation of Mechanophores

8.3.1 Ultrasound

Acoustic fields generated by an ultrasound transducer are the most common method to stretch dissolved polymers and the standard method used for testing polymer shear stability [25]. Putatively, the dissolved polymer is mechanically stressed by solvodynamic shear caused by the nucleation, growth and collapse of bubbles in solution. When a bubble is collapsing (implosion), the solvent and the dissolved polymer chains are pulled towards the forming cavity, resulting in elongational flow. The atoms closer to the bubble will move faster than those away from it, causing the polymer to uncoil. Due to the different relative motion of the polymer segments and small solvent molecules, shear stress is produced in the polymer chain (Figure 8.5) [26]. In homopolymers, the stress level can be described by a gaussian distribution with the polymer center as peak [27, 28]. Scission (bond cleavage) generally is achieved through high-energy sonication, occurring within the middle 15% of the chain [29].

The rate of mechanochemical reactions caused by acoustic fields increases with sonication intensity [30] and initial molecular weight of the polymer [31, 32]; but decreases with temperature [33], polymer concentration [26], viscosity [26], and vapor pressure of the solvent [34]. Other factors that influence the rate are polymer chemical composition [12] and architecture [18, 35, 36].

8.3.2 Tensile Testing

Studying the mechanochemical activation in the solid state is fundamental to the development of mechanophores for self-healing applications. Tensile testing is

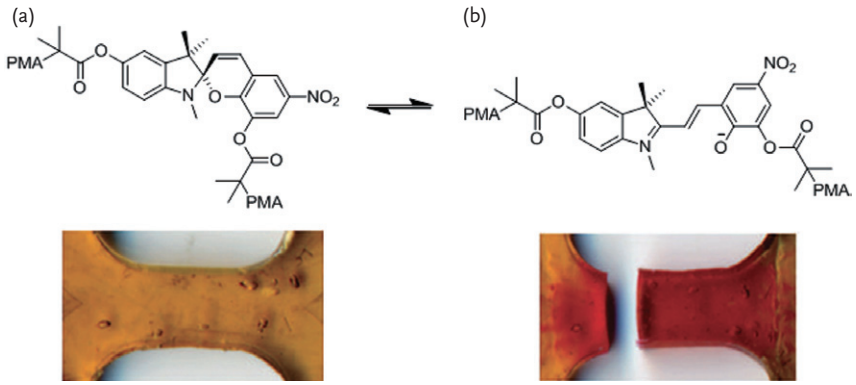


Figure 8.6 Dogbone samples of PMA-linked SP samples before (a) and after (b) stretching to failure [22].

one of the simplest and most effective ways to test mechanochemical activation through stretching solid samples of material. Tensile strains can be amplified in the area of a crack and may lead to its propagation, thus tensile testing is applicable to self-healing instances. Spiropyran (SP) was used as a mechanophore model in order to study the necessary conditions for mechanochemical activation during a stress–strain measurement [22]. This mechanophore undergoes a rearrangement to merocyanin (MC) which has a different color and is fluorescent, working as a probe for direct observation of the stress distribution in the solid material (Figure 8.6).

The stress state, as well as polymer mobility, are the most important factors to be considered for activating mechanophores in bulk polymers. In elastomers, stress levels are low and large deformations are necessary to achieve activation. As an example, when linear PMA ($T_g = 12\,°C$) was tested at room temperature, activation was observed only after several hundreds of percent strain. In glassy systems, where $T_{test} << T_g$, no activation is observed (and no yielding occurs). Significant mechanochemical activation was only achieved when test temperatures were below but close to T_g, and only after material yields, that is, plastic deformation is necessary in order to have mechanochemical changes [37]. Using linear PMMA ($T_g = 128\,°C$), a significant color change was observed during tensile testing between 90 and 105 °C, starting at as low as 10% strain. Interestingly, the authors demonstrated that reducing the T_g by the use of a plasticizer caused the temperature of effective mechanochemical activation to be reduced. The addition of 15% MeOH as a plasticizer to linear PMMA reduced its T_g to 80 °C and mechanochemical activation of SP was observed while stretching at room temperature.

Another important factor demonstrated using SP is the alignment of the mechanophores with the force direction. The dipole moment of MC groups can be used to measure their orientation via the anisotropy of fluorescence polarization [38]. Indeed, during tensile testing, the chains (and the mechanophore which is part of them) tend to align themselves with the force direction, especially in the places where stress is higher. This important work provides a mechanochemical method

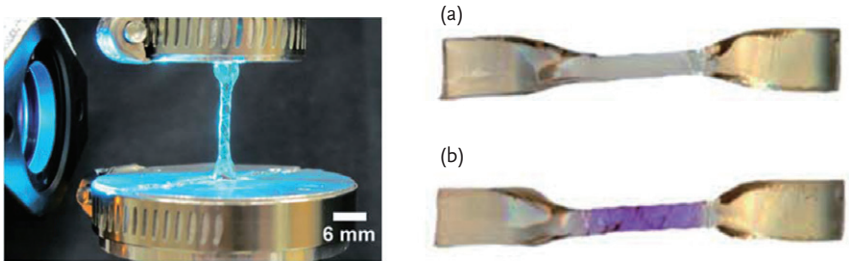


Figure 8.7 PMMA–EGDMA-SP samples before (a) and after (b) torsional testing [39]. Reproduced by permission of The Royal Society of Chemistry.

to ascertain both deformation (leading to chain alignment), and mechanophore activation (bond cleavage), and demonstrated that mechanochemical reaction is more significant when the chains are aligned with the force.

8.3.3 Torsional Shear Testing

Shear stress was used as a method to activate mechanophores in polymers. Using SP as a model mechanophore, a torsional (shear) strain was applied and was demonstrated to be very efficient for mechanophore activation, being able to cause yield and high stress before sample failure [39]. SP was used as a cross-linker in PMMA, and as in the case of tensile testing, mechanophore activation was observed only after the polymer yielded, again indicating that plastic deformation is necessary (Figure 8.7).

8.3.4 Compression

Compression is another common loading condition for solid state materials. Similarly to the previous cases, SP was used in order to study compression in mechanophore activation [22]. PMMA beads cross-linked with SP and ethyleneglycol dimethacrylate (EGDMA) were prepared by suspension radical polymerization, and compressed with a stepper actuator coupled to a load cell, which allowed strain rate control. The MC coloring was localized in the center of the spheres, regions of highest deformation and tensile stresses, indicating activation under diametric compressive loading is actually through tensile forces actuating transverse to the compression axis (Figure 8.8).

The advantage of this method is that large stresses are conveniently applied, allowing the activation of mechanophores which may be difficult to activate by tensile testing. For example, the exothermic ring-opening of *gem*-dihalocyclopropanes was demonstrated in linear polybutadiene, while no activation was observed during tensile testing [40]. The authors noticed that keeping the material under compressive loading for longer times did not lead to higher mechanophore activa-

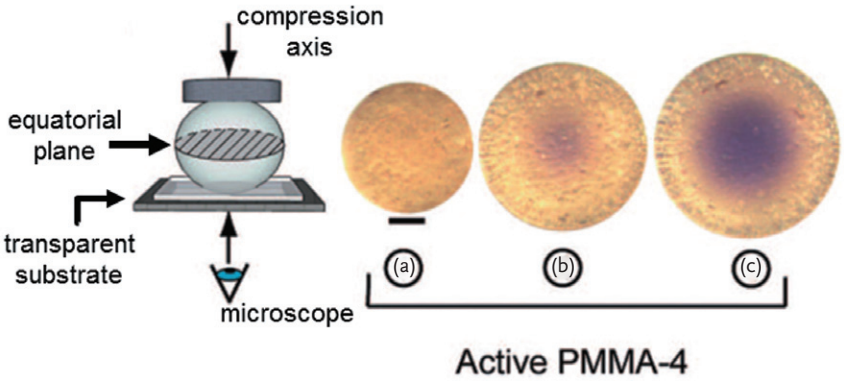


Figure 8.8 The sample configuration and experimental set-up for diametric compressive loading is illustrated schematically. Tensile forces develop in the equatorial plane normal to compression axis. Cross-linked PMMA-SP beads before (a), during (b), and after (c) compression [22].

tion, but folding and re-compressing to the same load did. This implies that the activation occurs during the initial application of load, coinciding with when plastic deformation and considerable polymer flow occurs.

8.3.5 Others

Several other methods for mechanically stressing materials have been used in order to study mechanochemistry of polymers. Classical examples are turbulent flow [41], elongational flow [42], and repeating freeze–thaw [43]. The disadvantages of these methods are that they are non-uniform and, thus, difficult to control/calculate the forces applied to the dissolved polymers. In contrast, ultrasound is simple to use, and, although it provides excessive mechanical energy, there are several parameters which can be changed in order to change the energy transferred to the chains (see above).

A modern and more sophisticated, precise method to apply force to a macromolecule is using single molecule force spectroscopy measurements (SMES) with the help of atomic force microscopy [44]. This method provides a precise measure of the force applied to the chain and, therefore, can be used to calculate the energy necessary for a mechanochemical reaction in a specific chain. On the other hand, force-induced structure changes cannot be validated by direct spectroscopic methods but rather, must be inferred indirectly. Another interesting method for activating mechanophores was the development of a molecular device where photoinduced geometry change causes stretching of the mechanophore [45]. This technique, while limited in mechanophore size, uses small molecules to apply mechanical force and allows simple chemical analysis, which is a challenging issue when studying mechanochemical reactions in macromolecules.

Finally, theoretical modeling of mechanical forces is a significant method to study mechanochemical reactions. For example, "constrained geometries simulate external force" (COGEF) is a simple method to predict the mechanochemical reaction products, and calculate activation energy and thermodynamic parameters [46]. More complicated, but more revealing theoretical studies include the combination of COGEF with "external force is explicitly included" (EFEI) [47], the combination of molecular dynamics with *ab initio* techniques [48] and others.

8.4 Mechanochemical Self-Healing Strategies

Mechanophores are promising functionalities for the development of self-healing materials. As described above, mechanical energy causes localized changes in the chemical structure, activating a materials system at the molecular level even before macroscopic failure. One of the first discovered mechanochemical reactions was the self-healing of vulcanized rubber. Damaging mechanical force, which is concentrated in the rubber's cross-linkages, cleaves several S–S bonds into long-lived reactive sulfur radicals that, in the absence of oxygen, recombine reforming the cross-linking bonds [7].

While self-healing is defined as the recovery of mechanical properties at the macroscopic level [49–51]; in this section, damage and healing are described at the molecular level; that is, mechanical damage leading to chemical bond cleavage, and healing systems based on chemical bond formation. It is important to emphasize that the cleavage of some chemical bonds does not necessarily affect the mechanical properties of the material. In addition, forming chemical bonds may change the material in different ways, not necessarily restoring the original mechanical properties, especially if the new chemical bonds are different from the bond cleaved by the mechanochemical damage.

Several mechanophores were not intentionally designed for self-healing applications but contain the basic chemistry to form new chemical bonds, and therefore have potential self-healing features. Using the serendipitous case of rubber as a model, mechanophores that produce reactive species under mechanical stress, with the possibility of reacting with a different chain to form new chemical bonds, provide a basic strategy. Improving on the original strategy, mechanophores that produce active catalysts instead of reactants can increase the healing effect by turnover. Finally, disrupting a chemical equilibrium with mechanical force provides a third strategy, where the system heals by reforming chemical bonds when the system re-equilibrates. These strategies are described in more detail in the following sections.

8.4.1 Production of Reactive Species

As described before, under high mechanical stress, covalent bonds may be cleaved homolytically in polymeric materials, producing two radicals. Radicals, as a highly

reactive species, may react with different surrounding molecules or decay through disproportionation or reaction with oxygen. This strategy works well with vulcanized rubber, since it has a high concentration of the mechanophore. The reactive species produced is long-lived in the absence of oxygen, and the material is soft enough that the chains have sufficient mobility to bring the reactive radicals together to form new bonds.

While the same kind of reaction (cleavage to radicals) can occur in most polymers, this unique self-healing feature is rare. For glassy polymers below T_g, mobility is limited and thus, the likelihood two radicals will meet and combine is small. In addition, in the case of polymers where carbon–carbon or carbon–heteroatom bonds compose the main chain, short-lived carbon radicals are produced, which tend to decay through non-productive chemistry. In order to get the same effect that was serendipitously incorporated in rubber, judiciously designed mechanophores that produce reactive species with longer life-times need to be incorporated.

Polyethyelene glycol having a single azo mechanophore per chain was used to study the effects of polymer molecular weight and mechanophore positioning on the mechanochemical reaction rate [52]. This mechanophore produces tertiary carbon radicals with an α-nitrile group, which are relatively long-lived radicals, used often for radical polymerization. When the azo group was released from the chain thermally (heating to 82 °C), recombination of the radicals was observed, indicating that the two radicals could potentially rebind and restore the chain's molecular weight. However, during sonication, the recombination product was not observed. Instead, a cyanohydrin was produced as the only product, probably from the reaction of the radical with oxygen or hydroxyl radical (Figure 8.9). The activation of this mechanophore was studied only in dilute solutions, and the

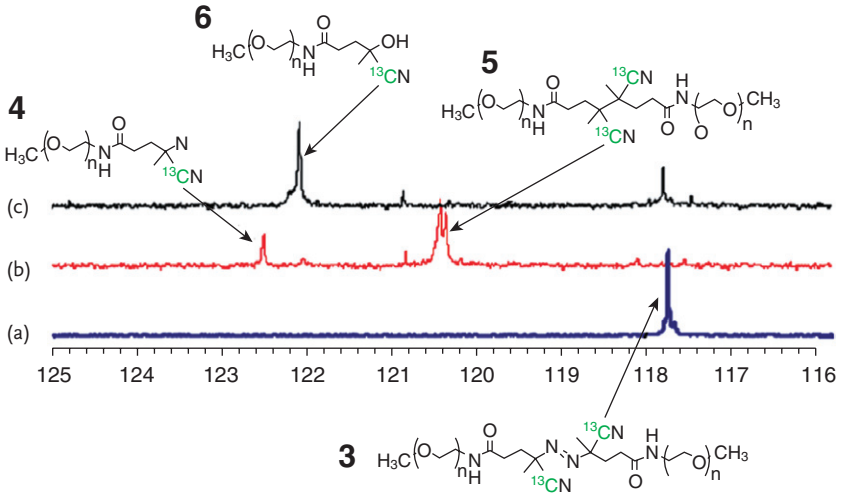
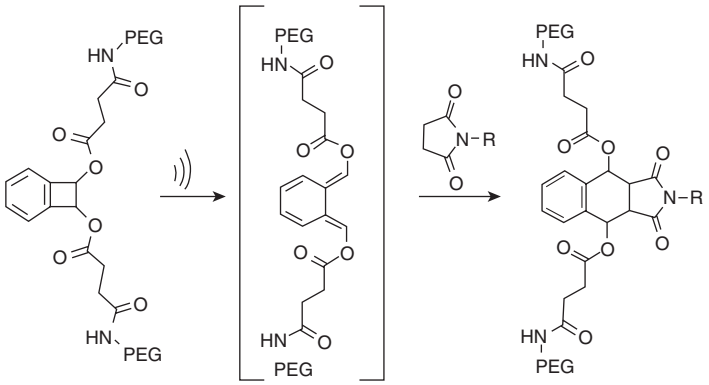


Figure 8.9 ^{13}C NMR spectra of (a) polymer 3, (b) thermal activation products 4 and 5, and (c) sonication product polymer 6 (c) [1, 52]. Reprinted with permission from reference [1]. Copyright 2009 American Chemical Society.

reaction pathway of this mechanophore in bulk polymers, where the concentration of the radicals is higher and access to water/oxygen limited, was not reported.

Strained cyclic molecules, such as cyclobutanes and cyclopropanes, were shown to selectively undergo ring-opening under mechanical force when incorporated close to the center of a polymer chain. Benzocyclobutene, for example, produces a reactive *ortho*-quinodimethide diene under sonication (Scheme 8.1) [13]. While the paper's focus was on the interesting fact that mechanical force can take a reaction to a different pathway compared to the thermal reaction, the identification of the reactive product was done by "trapping" using a Diels–Alder (DA) reaction, achieved by sonicating in the presence of excess of a dienophile. Several successful self-healing systems based on DA reactions have already been demonstrated (see Section 8.4.3); this mechanophore, which produces a very reactive diene, in combination with a polymer having dienophiles in side chains, may be developed into another successful system.

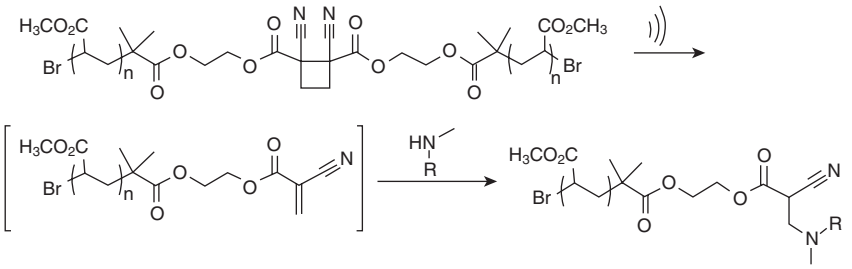


Scheme 8.1 Sonication of a polymer containing a chain center benzocyclobutene affording a reactive *ortho*-quinodimethide diene, which is trapped by a DA reaction with a dienophile [13].

Cyanoacrylates are a stable but very reactive functional group, and constitute the next attempt to develop a mechanophore which could be used for self-healing materials [53]. Using a substituted cyclobutane precursor as a mechanophore, sonication selectively cleaves the polymer into two chains of half the original size, each having one cyanoacrylate as a terminus (Scheme 8.2). Excess secondary amine as a trapping reagent confirmed the presence of cyanoacrylates, reacting only when sonication was started. A polymer having secondary amine side groups may produce new covalent bonds when the cyanoacrylates are released, but no report has been published.

8.4.2
Activation of Catalytic Species

The mechanochemical activation of catalysts stands by itself as a novel method for triggering latent catalysts. Polymers containing different catalysts were prepared,



Scheme 8.2 Production of reactive cyanoacrylates by sonication, and subsequent trapping with a secondary amine [53].

and shown to be inactive towards reagents until mechanical force (sonication) is applied [54, 55]. If the reagents for the activated reactions are part of the polymer side chains, catalyst activation under mechanical force could lead to cross-linking between chains. No example of this reaction has been reported yet, but several reactions using small molecule reagents were demonstrated in both solution and the solid state.

In 2008, a mechanophore was designed to undergo Bergman cyclization and generate radicals without causing scission to the polymer backbone [56]. This mechanophore was used as a cross-linker in PMMA and was mechanically activated by swelling in methyl methacrylate (MMA). Although the evidence was not fully conclusive, the findings suggest that swelling initiated the mechanochemical reaction, producing the desired di-radical. This, in turn, initiated the polymerization of the MMA. While not described as a self-healing system, this mechanophore catalyzed the production of new polymer chains around the mechanically stressed area (Figure 8.10).

Homogeneous organometallic complexes are the finest in chemical catalysis, achieving the best selectivities, turnover numbers and rates [57], making them suitable candidates for mechanically activated catalysts. The first study reported was a ruthenium olefin metathesis catalyst where two of the ligands are telechelic polymer chains [54]. Under mechanical force, the weaker ligand–metal bond is cleaved, leaving the metal with an open coordinating spot, effectively activating it (Scheme 8.3). As in the previous case, the authors were able to show that the activated catalyst can start a polymerization reaction [58]. Following this example, several other organometallic reagents were incorporated into polymers and shown to be activated only under mechanical force, such as palladium [59] which can catalyze several different carbon–carbon and carbon–heteroatom bond formations, and silver [54, 60] which can catalyze trans-esterification reactions.

Mechanical generation of less complex catalysts has the advantages of stability and lower costs compared to organometallic reagents. By cleaving a boronium–pyridine bond, a Brønsted base can be produced (Scheme 8.4) that is able to initiate the anionic polymerization of α-trifluoromethyl-2,2,2-trifluoroethyl acrylate [61].

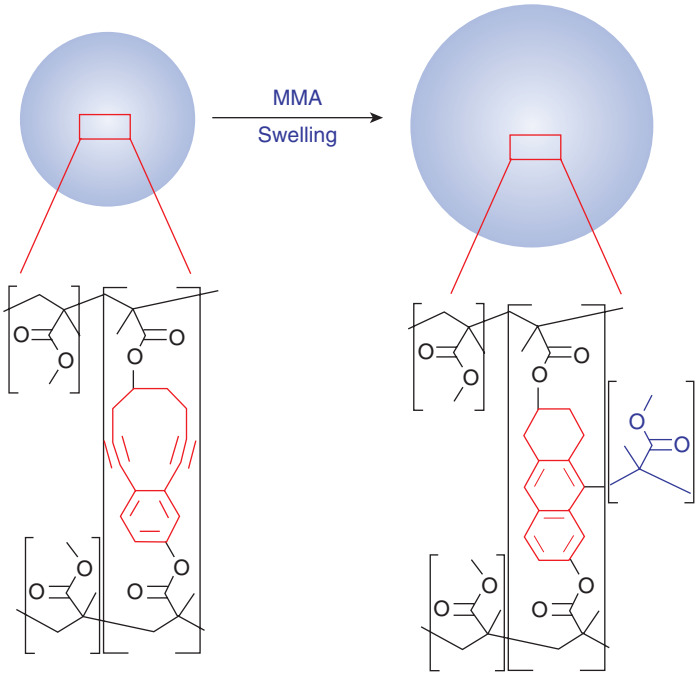
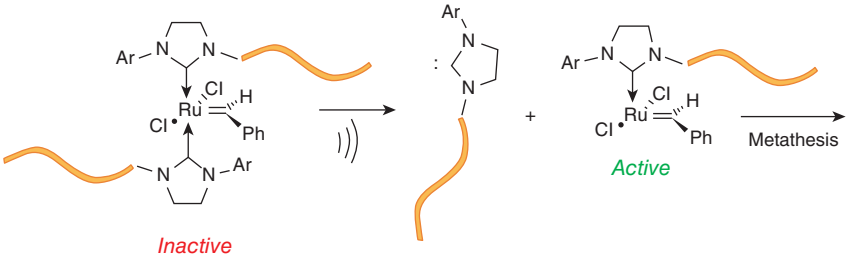
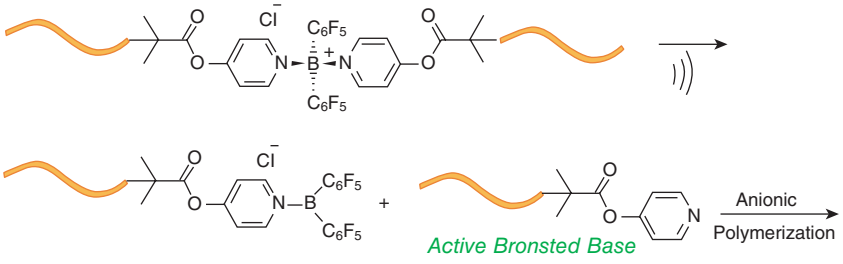


Figure 8.10 Swelling activation of a Bergman cyclization followed by radical polymerization [56].

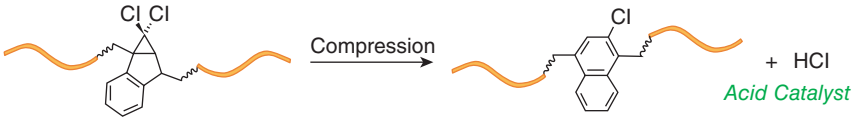


Scheme 8.3 Latent bis-NHC ruthenium olefin metathesis precatalysts activated by sonication [54].



Scheme 8.4 Anionic polymerization initiated by a Brønsted base, which is produced by sonication [61].

A drawback of the catalytic systems described above is that the activated catalysts are bound to a polymer chain, and therefore have very limited mobility in the solid state, which limits the turnover they are intended to achieve. In order to address this problem, an acid-releasing mechanophore was developed. The acid produced is not part of the polymer chain, but is released by elimination as a small molecule (Scheme 8.5) [62]. The inorganic acid has a larger mobility even in the solid state (as demonstrated in photoresists based on photoacid generators) and has the potential to catalyze different chemical reactions, including polymerizations.

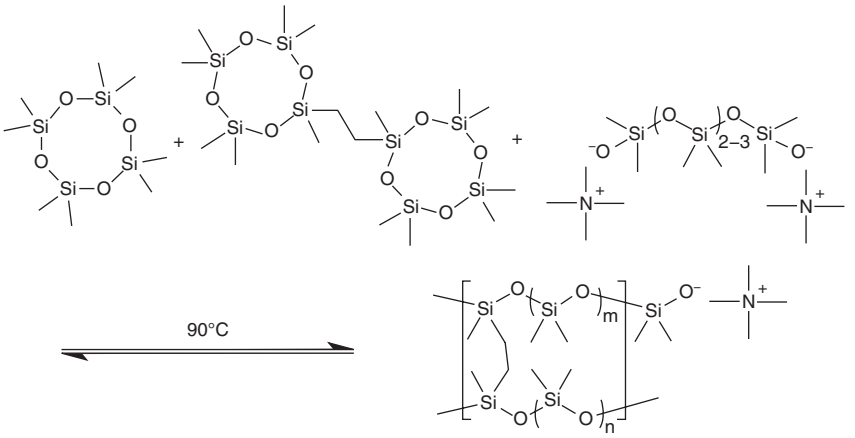


Scheme 8.5 Production of an inorganic acid by mechanical force, the acid is not bound to the polymer chain and may diffuse to reach numerous substrates [62].

8.4.3
Disruption of Equilibrium

Chemical equilibrium is the state in which both reactants and products are present at concentrations which have no further tendency to change with time [63]. When the equilibrium is disrupted, for example by partially cleaving chemical bonds and changing the concentrations of the different components, the system presents a chemical potential to return to the equilibrated state.

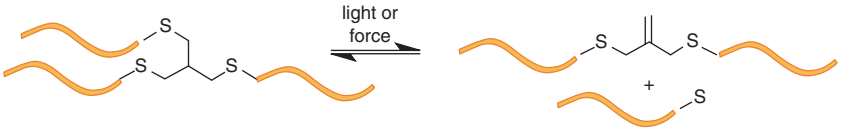
Living polymerizations in which the propagating species is relatively stable towards the environment is one approach to using chemical equilibrium as a method to heal polymers. In the 1950s, cross-linked polydimethylsiloxane (PDMS)–described in Scheme 8.6–was prepared by anionic polymerization [65].



Scheme 8.6 Equilibrium between cyclic monomer and linear oligomers in anionic polymerization to produce cross-linked PDMS [64].

The system contains tetramethylammonium dimethylsilanolate termini as propagating species, which are stable towards air and water. During polymerization at 90 °C, the system equilibrates between linear chains, cross-linkers and cyclic oligomers [66]. If covalent bonds on the linear chains are cleaved by mechanical damage, the equilibrium between the constituents is disrupted, meaning that, given the conditions where they have enough mobility to react, the system will re-equilibrate by sacrificing cyclic oligomers to reform linear chains. Heating the damaged polymer for 24 h causes complete healing of the system [64].

In a similar approach, cross-linked networks made by thiol-ene polymerization undergo chemical changes to adapt to imposed mechanical stress, without losing mechanical properties [67]. When irradiated (320 to 500 nm, 30 mW cm^{-2}) the thioether groups can undergo reversible addition–fragmentation through a sulfur radical mechanism, effectively moving the covalent bonds through the irradiated area (Scheme 8.7). Using a polymer that contains a large quantity of thioether groups, it was demonstrated that the material could keep constant mechanical properties while being deformed and irradiated.

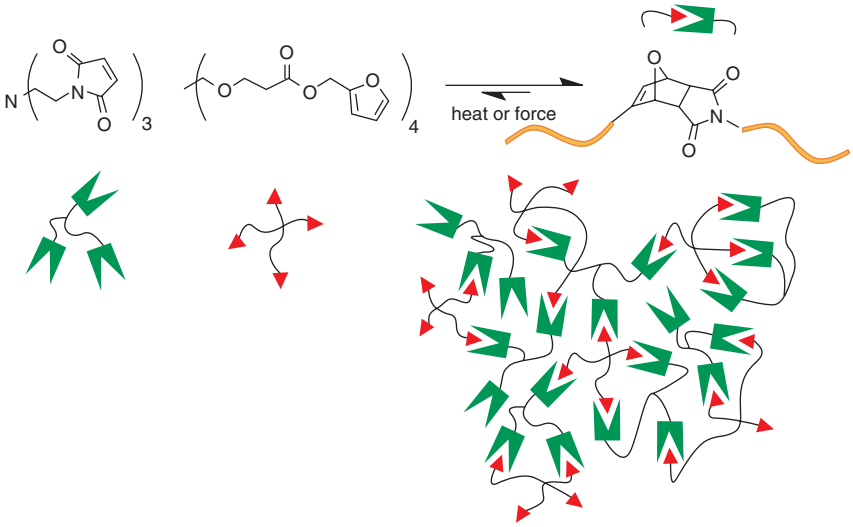


Scheme 8.7 Reversible fragmentation (caused by light or mechanical force)-addition in thioether containing polymers [67].

This strategy was recently expanded by post-polymerization addition of catalysts that allow the metathesis of strong covalent bonds. In these materials, the bonds re-equilibrate as directed by the mechanical potential. For example, transesterification of cross-linked epoxies at high temperatures is possible by addition of $Zn(acac)_2$, allowing this "thermoset" to be molded or mended, while maintaining its strong mechanical properties upon return to room temperature [68].

Addition of a small quantity of Grubbs catalyst to cross-linked polybutadiene allows room-temperature metathesis of the double bonds in the polymer backbone [69]. Mechanical stress applied to this material triggers metathesis between the chains, causing the strain to increase constantly with time at constant stress, or the dissipation of the stress at constant strain.

The second approach to equilibrium-based healing is centered on systems where the bound state is more energetically stable than the unbound state, but the unbound state is long-lived and mostly unreactive towards other reagents in the system. The original idea was demonstrated for the cross-linked polymer shown in Scheme 8.8, prepared by DA reaction [70]. Interestingly, this material has mechanical properties similar to epoxy resins. A crack was induced in the material and healed by a heating/cooling cycle. During the heating period, the equilibrium is disrupted toward the reagents, while during a slow cooling these would react again in their new position, mending the crack. However, the authors did not know at that time that mechanical damage by itself is enough to break DA products

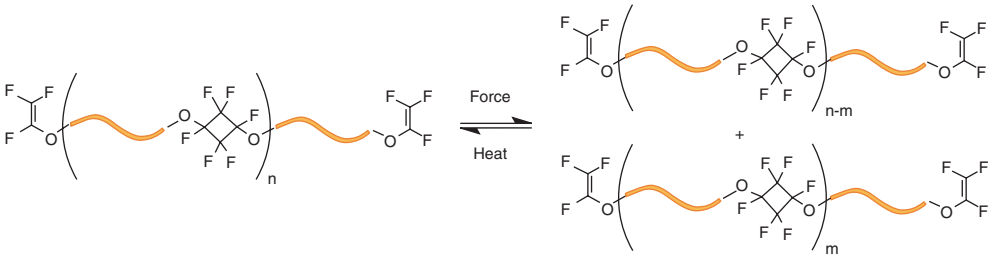


Scheme 8.8 Reversible DA reaction in cross-links of a polymer network [70].

into their reagents, as demonstrated several years later [71]. While heating is still necessary (increases chain mobility, activation energy), a high concentration of "reagents" was already present on the surface of the crack.

This approach was also shown to work for other cycloadditions. A crack was induced in a thermoset prepared by photochemical [2+2] cycloaddition of a tris-cinnamoyl monomer [72]. Assuming most mechanochemical damage was cyclobutane cleavage, the material was healed by photoirradiation to re-form the cyclobutanes. Better healing was achieved when the photoirradiation was conducted under heating, however, heating alone did not provide any healing.

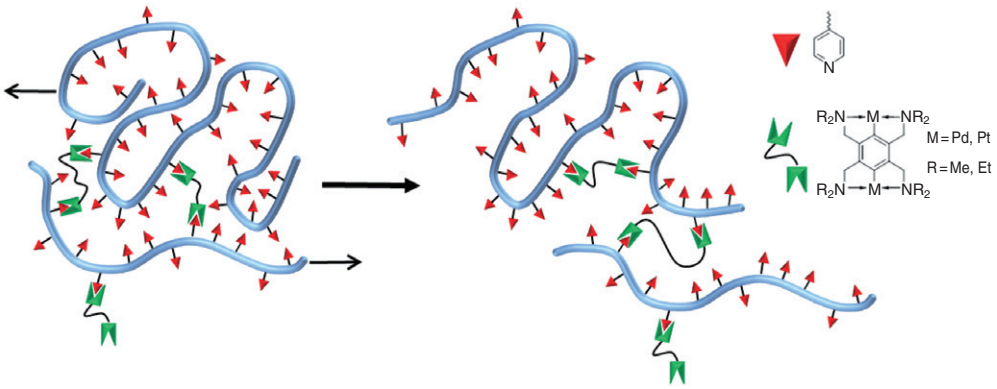
This strategy works also in linear soft thermoplastics. A perfluorocyclobutane aryl ether polymer was prepared by step-growth [2+2] cycloaddition containing several mechanophores along the chains [73]. Mechanical force induced the retro [2+2] cycloaddition into shorter linear segments with trifluorovinyl ether termini. These, given enough energy, can rebind, mending the linear chains (Scheme 8.9). Interestingly, the linear chains do not necessarily return to their original size – the



Scheme 8.9 Reversible cycloaddition of trifluorovinyl groups to form and cleave a linear thermoplastic [73].

size of the product depends on the equilibrium between open and closed forms, which depends on concentration and temperature.

Weaker non-covalent bonds were used as an alternative to cycloaddition reactions. Poly(4-vinylpyridine) (PVP) was cross-linked by addition of Pd or Pt (Scheme 8.10) [74]. The authors demonstrated that these cross-linkers bound reversibly, changing between inter and intra-chain cross-links in accordance to the mechanical stress. In another example, a telechelic polytetrahydrofuran with terminal phosphines was used to make networks using rhodium and iridium, each metal binding up to four different phosphines [75]. These systems undergo sol–gel transition under sonication, but given enough time, revert to the original state.



Scheme 8.10 Cross-linking of PVP by organometallic complexes forming reversible coordinative bonds [74].

Supramolecular polymers held together by hydrogen bonds make efficient self-healing systems. A rubber-like polymer formed from polyfunctional carboxylic acids and diethylenetriamine further functionalized with urea could be cut and rebound [76]. If the two pieces were immediately rejoined, complete recovery of some mechanical properties was achieved. Healing efficiency was decreased if the parts were rejoined after a delay, supposedly as a consequence of new hydrogen bonds re-formed in the separate parts.

8.5 Conclusions and Outlook

Modern mechanochemistry, the development of productive chemistry by mechanical stimuli, is a relatively new scientific direction with the potential to impact several technologies. The development of mechanochemically activated self-healing systems is just one of the various applications under development. The mechanophore concept allowed localization of the mechanical force into selective chemical reactions, and the production of high energy intermediates which are

able to form new chemical bonds. The study of mechanophores in solution allows an easy and fast screening of new mechanophores, while their study in the solid state is useful in the direct observation of mechanical stress in materials, as well as the simulation of the materials' response to damaging mechanical stress.

The biggest limitation to a mechanochemical self-healing system is the activation in the solid state, which is constrained to certain environmental conditions, directly related to the T_g of the material. On the other hand, a mechanochemical system can be incorporated into a material without changing its mechanical properties, which is a limitation when using larger scale self-healing systems. Mechanophores display a homogeneous distribution throughout the material, and actuate at the molecular level even before a crack is produced, restricting their effect to the places where mechanical stress is maximized.

Several self-healing systems based on mechanochemistry have already been reported and were described here. A challenge still unmet by mechanophores is in the development of an autonomic self-healing system, where the mechanical energy will initiate the cascade which eventually leads to chemical bond formation without any additional energy or human intervention. An autonomic self-healing mechanochemical system will give access to the ultimate self-healing material, which will expand the lifetime of structural materials by maintaining their mechanical properties and adapting itself to the changes in mechanical stress.

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